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Some investigations on Porcelains for high tension insulators

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SOME INVESTIGATIONS ON PORCELAINS FOR HIGH TENSION INSULATORS

BY

BARNEY SIMONSON RADCLIFFE
A. B. Miami University, 1908

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CERAMICS

IN

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June, 4th., 1910

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Barney Simonson Ratcliffe.

ENTITLED Some Investigations on Porcelains for High Tension Insulators.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Science in Ceramics.

R. T. Stull.
In Charge of Major Work

C. W. Rolfe
Head of Department

Recommendation concurred in:

Committee
on
Final Examination

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Considerable investigation has been done on "Porcelains" but literature on the subject of "Electrical Porcelains" is comparatively meager and incomplete.

A. S. Watts(1) in his work attempted to show the effect of the alkalies and alkali earths on the di-electric strength of Porcelain Insulators but did not carry it far enough to determine their effect when the bodies were vitrified, except in the case of K_2O and CaO and concludes that a body composed of these two substances when added as feldspar and whiting together with kaolin and flint make~~s~~ the best insulator.

He also states that the di-electric strength increases as vitrification increases up to the point where the body loses its shape from overfiring.

A. Zoellner(2) in an article on "Porcelain as an Insulator from the standpoint of Physical Chemistry" claims that the firing is the important part of the manufacture. He advocates two burns.

The first heating (700 degrees to 800 degrees) drives off the combined H_2O and permits the quartz to spread throughout the mass, the quartz being sintered and strongly hygroscopic. It is then dipped in the glaze and burned to 1370 degrees or 1400 degrees C. At this temperature the mixture forming a glassy silicate and a crystalline silicate of the composition $Al_2O_3SiO_2$ called Sillimanite.

He says a good Insulator must show high transparency in thin pieces, a bluish appearance and a glossy fracture.

A. V. Bleininger and R. T. Stull(3) in their paper, "A study of the Vitrification Range and Di-electric Behavior of some Porcelains", conclude that high di-electric strength is a matter of through vitrification. As near as the writer has been able to learn the range

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(1) See reference at end of article.

of temperature in commercial work usually varies from cone 10 to 14 for high tension insulators.

The porcelains burned below this temperature are higher in alkalies and alkali earths than high fire Insulators.

(4) It is conceeded that the higher alkali content a glass contains the more hygroscopic the surface becomes which of course permits a greater leakage of current.

It is generally believed that a high temperature is necessary since low fire porcelains show a low di-electric strength.

The question remains whether the strength is a matter of composition or maturing temperature. If it is a question of vitrification then any cheap colored clay which will mature properly will be equally as good as a high fire mixture.

If the fracture and appearance of the body are in any way indicators of its strength then the composition and burning must be adjusted so as to produce the best bodies.

The following investigations were undertaken with the view of throwing more light on the points under discussion.

1. Determination of the relation between Di-electric Strength and Thickness.

2. The effect of varied heat treatment during the burning and cooling of the Porcelains.

3. Investigation of the value of Fire-clays as raw materials for high tension Insulators.

4. Influence of composition on the Di-electric Strength.

"Relation between Di-electric Strength and Thickness".

There is no generally accepted method for calculating the

Voltage per unit Thickness. Some hold that it is directly proportional to the thickness while others think it is proportional to the square of the thickness.

The strength of insulating material such as varnished and impregnated papers is, in most instances proportional to the square of the thickness. Para is an exception and its strength is directly proportional to the thickness.

Since no reliable data on this subject relating to Porcelains could be found, it was decided to construct a body which would vitrify at cone 12, vary the thickness of the trials, burn and puncture them and thus calculate the relation between the two factors.

For this purpose a body having the folowing composition was used.

Tenn. Ball Clay No.1-----------15 parts.
N. Carolina, Kaolin-----------20 " .
Eng. China Clay----------------25 " .
Spar (Brandywine Summit)------20 " .
Flint (Ohio 8 Hr. Grind)-----20 " .
Total-------------------------100 " .

The mixture was blunged for about 10 hours, screened through a 120 mesh sieve and poured into plaster molds. When it became dry enough to handle it was removed from the molds and wedged for about five minutes on a plaster slab.

Trials were made by jiggering. They were crock-shaped, being $2\frac{7}{8}$ inches in diameter and 1 inch deep, Fig.1. Thickness, between 1.4 and 7 millimeters.

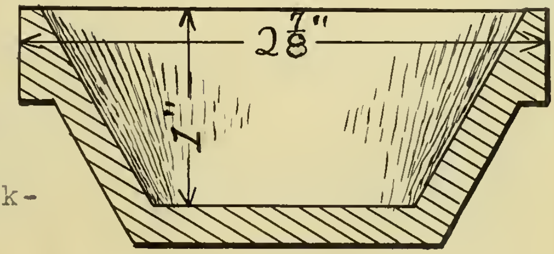


Fig. 1.

After drying, the trials were burned to cone 12½, in the Stull-Knote(5) down draft muffle gas-furnace. The time required for burning, being about six hours.

At this temperature the bodies were all well vitrified.

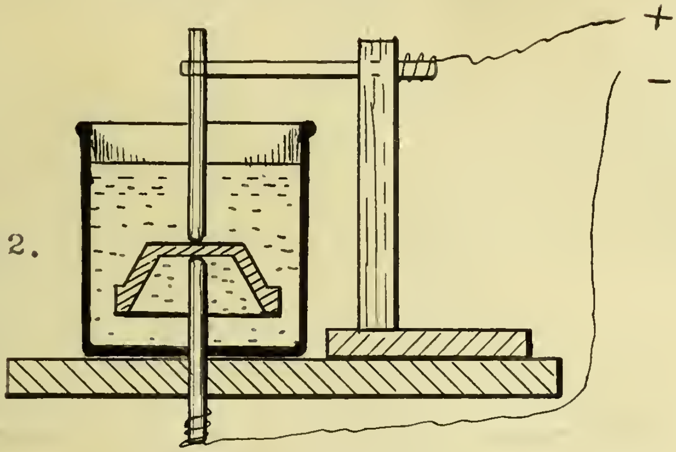


Fig. 2.

2

The pieces were placed between copper electrodes submerged in transformer oil and the current turned on, Fig. 2. By gradually cutting out the resistance of a rheostat the voltage is increased accordingly until the trial is punctured, after which the circuit is immediately broken. The thickness in millimeters at the point of puncture is measured with a ~~spher~~micrometer and from this data the voltage-thickness relation is calculated.

Five to ten trials for each thickness were tested and the average voltage of the series was taken as the true di-electric strength.

Thick. in MM.	Voltage.
1.80	29,600
2.27	34,900
2.61	40,000
3.20	47,600
3.76	55,500
4.21	56,700

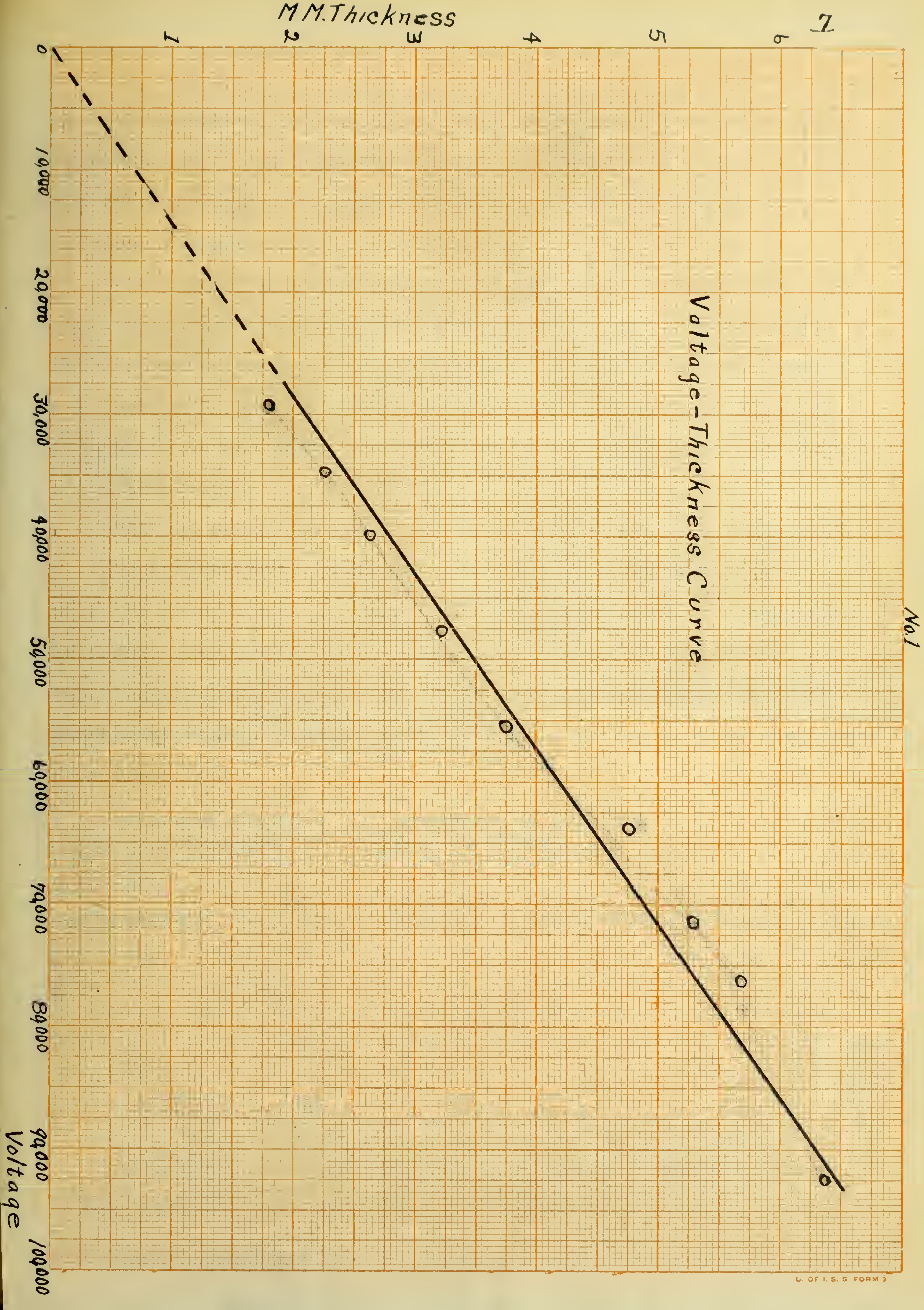
Thick. in mm.(Cont'd)	Voltage.(Cont'd)
4.86	63,500
5.29	71,500
5.70	78,800
6.30	92,000

By observing curve number 1 on which Thickness is represented by the ordinate, and Voltage by the abcissa we see that the Voltage required to puncture the trials is approximately proportional to the Thickness.

By exterpolating the curve from 1.8mm. down to zero thickness (represented by the dotted line), we find that it passes through the point which indicates approximately 14,000 volts per mm. thickness which is the average voltage per millimeter thickness required to puncture the entire series.

Owing to lack of apparatus for testing trials of greater thickness, the investigation could not be carried farther but the limits exceed the requirments in the future tests, and is, therefore, sufficient for the work at hand.

Some interesting results were obtained by puncturing the same test piece two or more times in the same spot. One piece which was 5.7 mm. thick and required 83,800 volts to puncture it, was given a second test and stood 79,000 volts, a third test required 59,300, a fourth 51,200 and when the trial was shifted so that the current passed through in a new place the voltage required to puncture it was 77,500 ~~volts~~. A few other trials were treated in the same manner with similar results. Repeated puncturing through the same line of puncture, without shifting the porcelain, apparently weakened the di-electric strength at that point but not until after



Voltage-Thickness Curve

No.1

several punctures did the piece become too weak to resist a fairly high voltage. And when the current had to pass through a new part, the voltage required to puncture it was almost as high as that originally required.

There is no adequate explanation for these facts but it seems that the current which passes after the piece is punctured heats up the part sufficiently for the molecules topartly readjust themselves and thus leave the piece only slightly weakened. Upon breaking the pieces at the point of puncture a glassy appearance was noticed which showed that the part had been fused.

"Effect of Varied Heat Treatment During Burning and Cooling".

It is generally conceeded that a Porcelain must be vitrified in order to be of value for high tension Insulators but no data could be found which compared the di-electric strengths of like bodies which had been variously burned and cooled, so four of the best porcelains from a previous (3) work were selected and a fifth compounded from these four.

The composition of the bodies is as follows:

No.	Ga.Kaolin.	No.1 Tenn.Ball.	N.Carolina Kaolin.	English China Clay.	Spar Brandywine Summit.	Flint.
A	50				40	10
B		55			15	30
C			55		25	20
D				60	20	20
E	5	9	27	18	23	18

Another set was made in which Soda Spar was substituted for Potash Spar of the above bodies, the substitution being molecule

for molecule.

This series was numbered A1, B1, C1, D1, and E1.

Twenty trials of each body of the two series were made. These were divided into four parts of five pieces each and burned.

Part (1) was burned to cone 10 in 6 hours, oxidizing conditions being mantained throughout the burn.

Part (2) was burned to cone 13 in 6 hours. Reducing conditions were mantained at the end of the burn, and, after completing the burning, a current of air was passed through the furnace which reduced the temperature to about cone 02 within an hour, after which the cooling went on naturally.

Part (3) was heated to cone 10 in 6 hours, the temperature was then gradually raised to cone 12 in an additional 14 hours, after which it was carried along rapidly to cone 17 where it was held for 2 hours with a reducing atmosphere. It was allowed to cool under normal conditions.

Part (4) was burned to cone 10 in 6 hours, gradually raised to cone 13 by the end of 24 hours, at which temperature it was held for 20 hours, after which it was cooled gradually to cone 2 in 5 hours, when the heat was withdrawn and the furnace left to cool gradually.

It was thought that a prolonged heating at the maturing temperature with slow cooling might encourage the formation of sillimanite crystals, while a rapid burning and cooling would tend to prevent their formation.

C and C1 of Part (1) had a porosity of about two percent but all of the other bodies were well vitrified and had an excellent white appearance.

Voltage permm. required to Puncture Trials.

	10 Part 1.	12 Part 2.	11 Part3.	13 Part 4.
A	13,260	13,120	12,600	13,070
A1	12,840	13,100	14,300	13,870
B	13,400	13,000	13,500	13,000
B1	14,000	13,640	13,620	14,160
C	10,320	13,960	12,760	13,180
C1	9,180	13,220	13,820	13,860
D	14,540	13,150	13,680	14,100
D1	13,400	13,920	13,100	13,520
E	13,550	13,470	14,660	12,850
E1	13,560	14,820	14,100	13,860

The above data shows the average voltage per millimeter thick- required to puncture the Porcelains, five trials of each body having been tested at each temperature.

These results show:

(1) That the Soda-spar bodies, taken as a whole, have a greater di-electric strength than the Potash-spar bodies.

(2) That the bodies, when varied through a temperature range of seven cones after complete vitrification, possessed practically the same di-electric strength.

This result is what one would expect however, because the homogeniety of the body, which is supposed to make glass stronger than porcelain, would not be sufficiently changed before fusion to make an appreciable difference in the strength of the body.

(3) That a quick burned and rapidly cooled body is as good as one which is given a long soaking heat with gradual cooling.

"Fire-clays as Raw Materials for High Tension Insulators".

The trade requires a white porcelain for Electrical Insulators and the belief is that the whiter the body, the stronger it is.

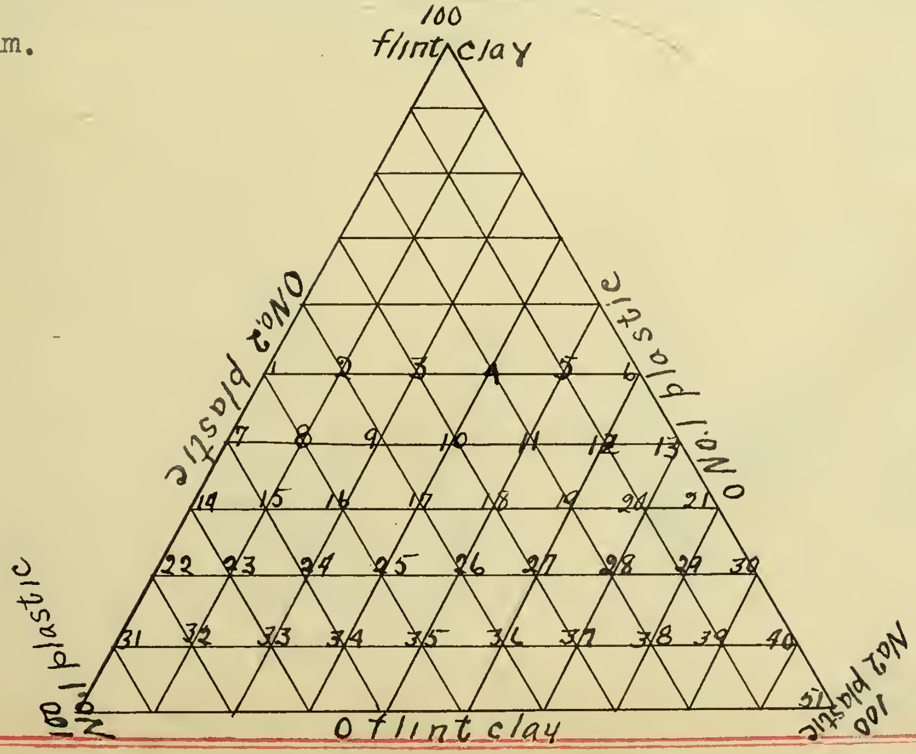
There is no data available concerning the use of colored clays for the manufacture of Insulators and it was thought that fire-clays which have practically the same composition as white burning clays might be just as good for this purpose.

An excellent No.2 fire-clay or stone ware clay was obtained from Bloomingdale, Indiana, and the flint and No.1 plastic fire-clays used, are pure variety which came from Olive Hill, Kentucky.

The flint clay was calcined in order to decrease its shrinkage after which it was ground in a porcelain-lined ball-mill until about half of it would pass through an 80 mesh and the remainder through a 40 mesh screen.

The plastic fire-clays were ground until they passed the 120 mesh screen.

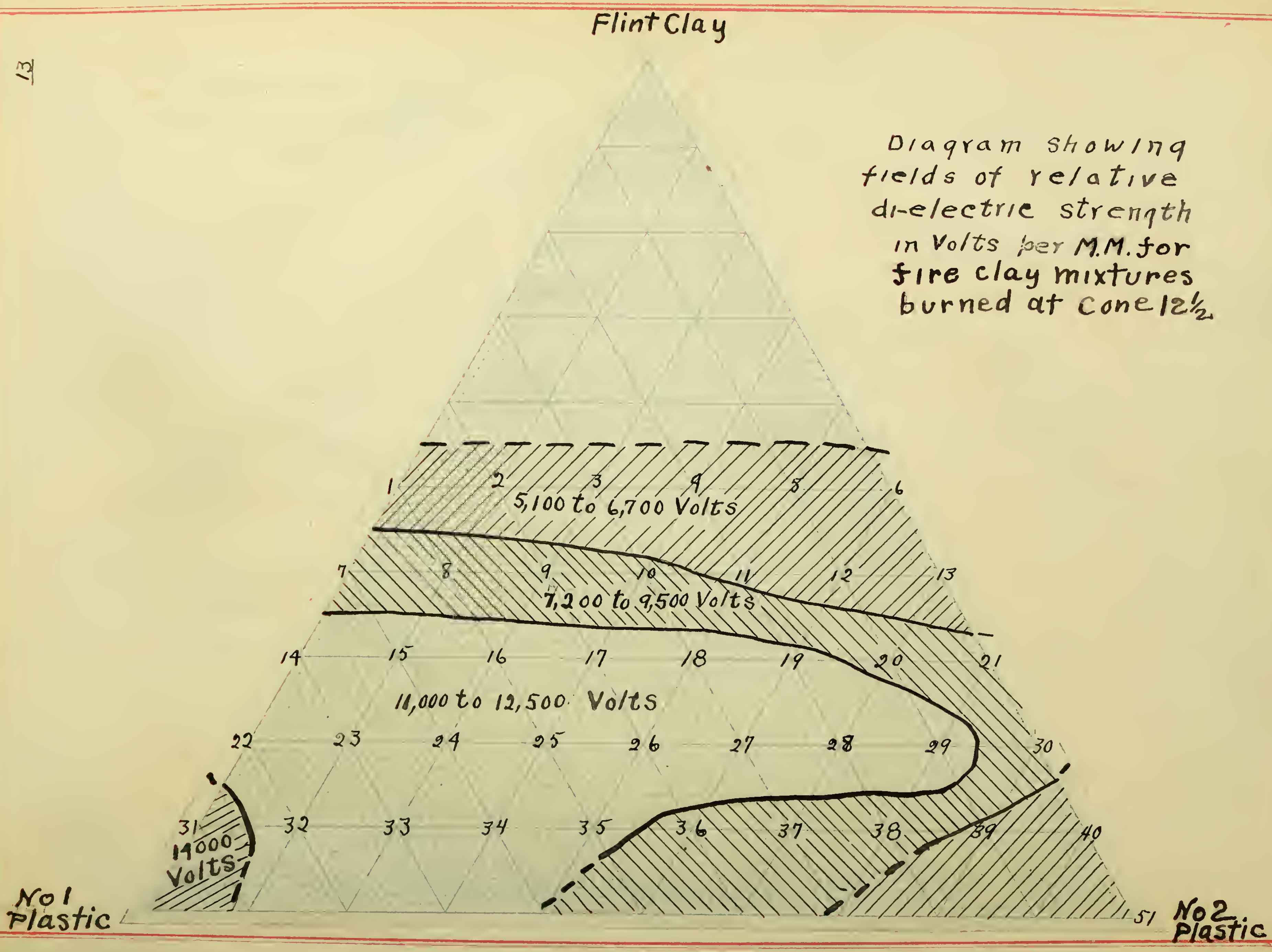
The bodies were blended wet, according to the following triangle diagram.


100
flint clay
0 No2 plastic
No2 plastic
0 No.1 plastic
No.1 plastic
1 2 3 4 5 6
7 8 9 10 11 12 13
14 15 16 17 18 19 20 21
22 23 24 25 26 27 28 29 30
31 32 33 34 35 36 37 38 39 40
100 No1 plastic
0 flint clay
100 No2 plastic

The upper part of the flint fire-clay series was not made because it was known that they would not be vitrified at cone 12 or 14 and that is about as high as it is practical to burn Insulators.

Five trials of each mixture were made and burned to cone 12½ with the following results:

No.	Por. in Percent.	Voltage per mm.	No.	Por. in Percent.	Voltage per mm.
1	22.80	6,100	22	1.40	12,100
2	23.50	5,600	23	1.77	12,000
3	22.10	5,100	24	1.60	12,400
4	23.05	5,400	25	2.70	12,500
5	23.00	5,100	26	2.84	12,400
6	21.28	6,700	27	4.75	12,300
7	14.65	8,050	28	5.82	12,200
8	16.75	8,100	29	7.70	11,100
9	17.92	7,300	30	9.20	9,000
10	18.12	7,200	31	1.00	14,000
11	18.35	6,100	32	.82	12,500
12	18.20	5,800	33	.43	13,000
13	18.30	6,100	34	.47	12,800
14	5.00	11,400	35	.53	12,000
15	5.50	11,450	36	.10	9,500
16	7.21	11,900	37	.06	8,000
17	8.52	11,000	38	.20	7,500
18	8.63	12,200	39	.04	5,500
19	11.26	12,100	40	.00	5,900
20	14.02	8,340	51	.00	5,400
21	13.32	8,200			


Flint Clay
No 1 Plastic
No 2 Plastic
5,100 to 6,700 Volts
7,200 to 9,500 Volts
11,000 to 12,500 Volts
14000 Volts
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
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40
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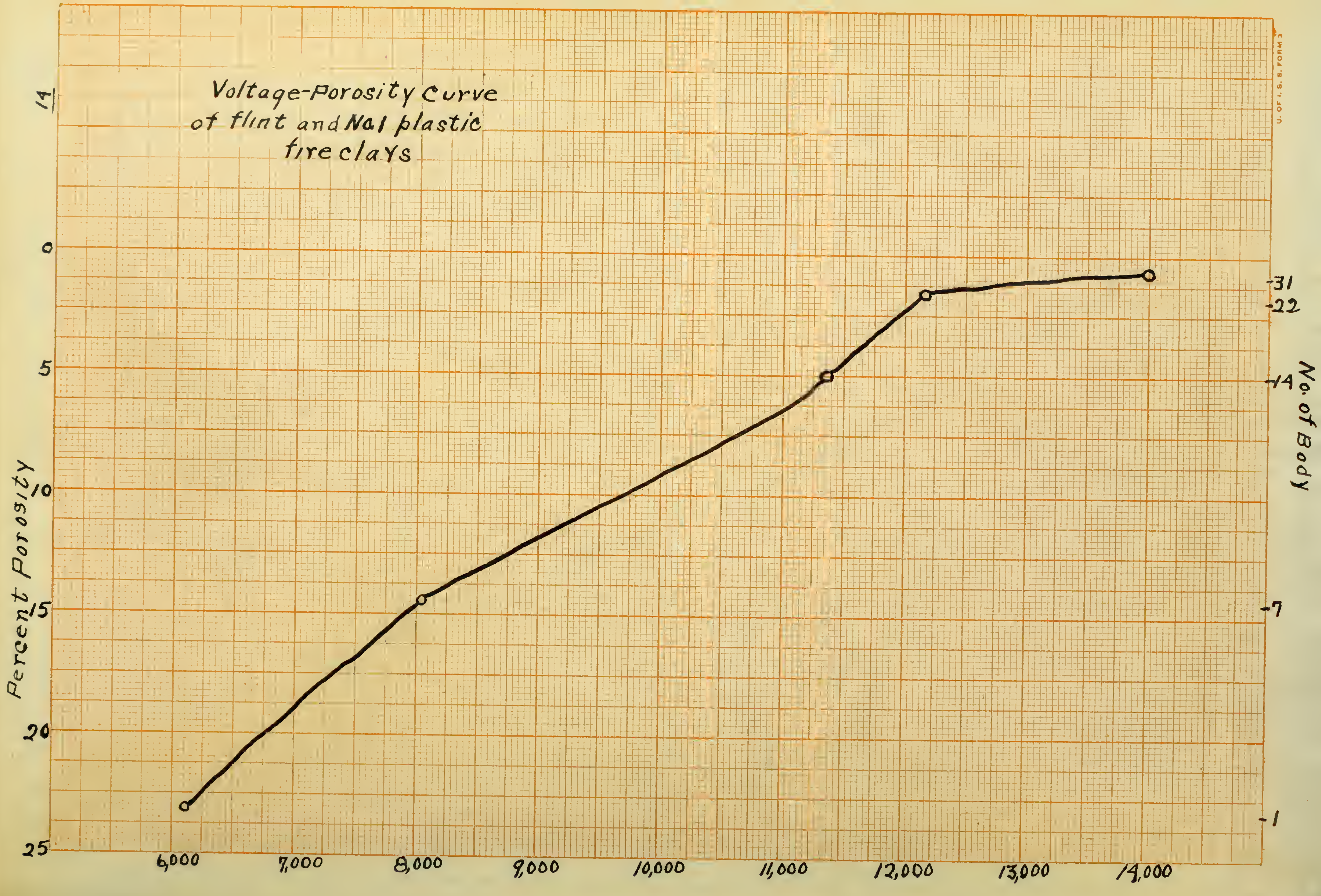
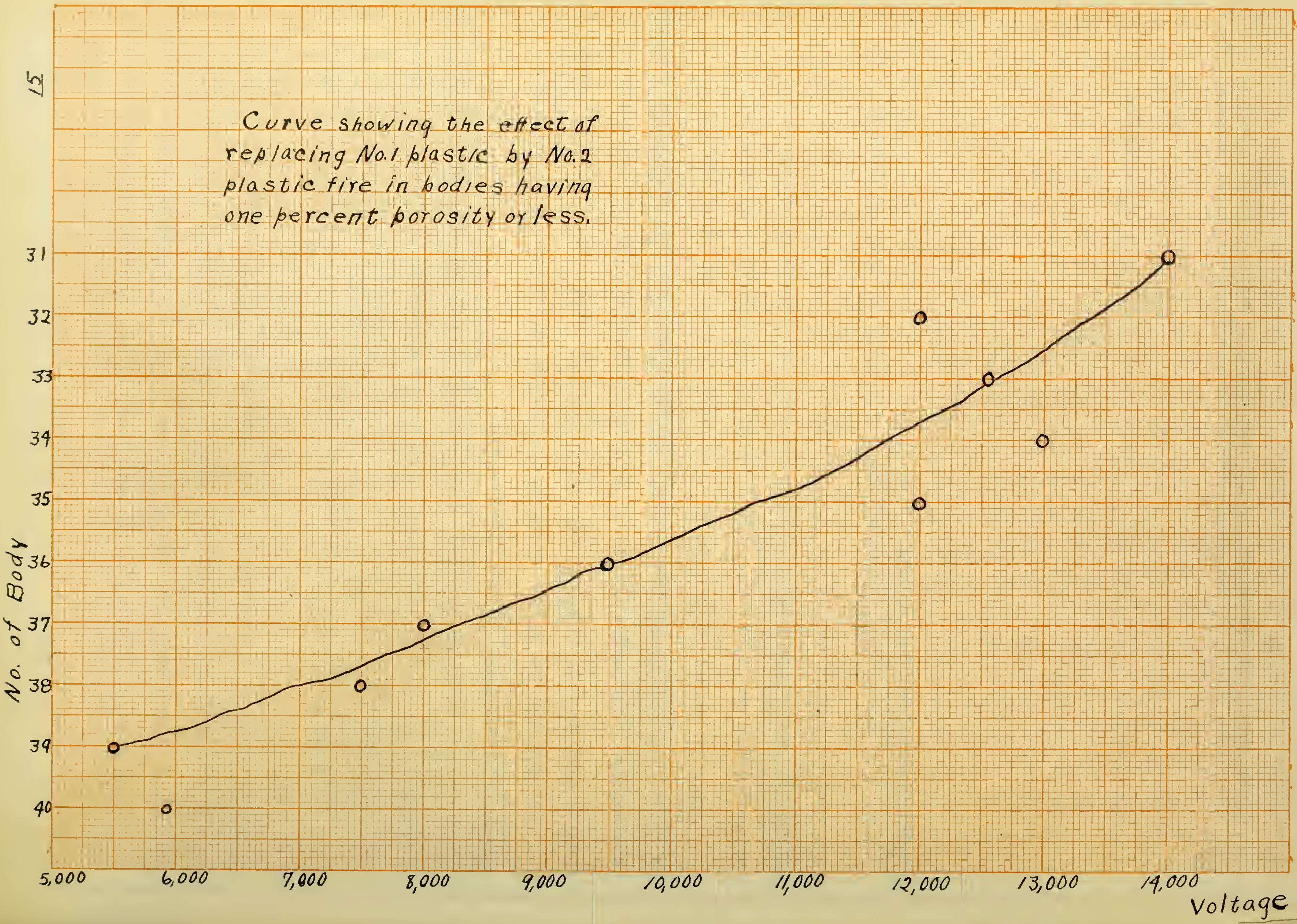
Diagram showing fields of relative di-electric strength in Volts per M.M. for fire clay mixtures burned at Cone 12½

14



Curve, showing that high flint fireclay makes a porous & hence a weak voltage resisting body.



Curve showing the effect of replacing No. 1 plastic by No. 2 plastic fire in bodies having one percent porosity or less.

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The results show that 10 parts flint and 90 parts No.1 plastic fire-clay give the best results at cone 12 and although these bodies have a porosity of one percent they conpare favorably with Porcelains, 14,000 volts per millimeter thickness being required to puncture them.

When No.2 plastic fire-clay is used to replace the No. 1 plastic fire-clay, and the flint clay is kept constant, the porosity increases in all of the bodies, except 31 to 40 of the series which shows that a mixture of the three does not combine well and would require a higher maturing temperature.

In the series 31 to 40 which contains 10% flint clay we see that although the porosity of the bodies is below one percent, there is a decided decrease in the di-electric strength as No. 2 plastic is used to replace theNo.1 plastic fire-clay.

Cone 12 seems to be too high a temperature to burn the No.2 fire-clay and as it is increased above fifty percent there is a marked tendency for blebs to form in the bodies which makes them weak and of little value for Insulators.

Bodies 14, 22 and 31 were burned to cone 14 and tested for porosity and di-electric strength

No.	Porosity.	Voltage per mm.
14	1.34	13,600
22	.08	14,100
31	.00	14,600

The results show that the flint and No.1 plastic fire-clays are equally as valuable for the manufacture of high tension Insulators as Porcelains when they are burned to the point of complete vitrification. Cone 14 is a high temperature for burning, but

the maturing temperature can be readily lowered by the addition of a flux such as soda or potash spar.

The writer is of the opinion that a body composed of No.1 fire-clay (about 25 percent of which should be calcined) together with from 10 to 20% of spar would make a better body than a mixture of the flint clay, No.1 plastic clay and spar since the flint clay is highly refractory and would thus require a larger amount of flux to make the body vitrify.

From a practical standpoint, it seems that a high grade plastic fire-clay body had quite an advantage over Porcelains because it would have a wider range of maturing temperature which would obviouslydecrease the kiln loses. The buff color would also be an advantage in securing a uniformily colored brown glaze which is extensively used on Insulators.

Fire-clay is also cheaper, more widely distributed and is usually located in favorable manufacturing districts.

"Influence of Composition on the Di-electric Strength"

If high di-electric strength depends upon the porcelain being well vitrified and not upon the composition as some writers hold, then it would be reasonable to assume that well vitrified porcelains whose fluxing agents were alkali earths or other bases would resist puncture equally as well as the feldspar porcelains.

It was thought that if a series of bodies were made which would vitrify at about cone 12, in which $CaCO_3$, $BaCO_3$, $MgCO_3$, and ZnO respectively were added as fluxes, a variety of porcelains would be obtained whose composition and specific gravities would be sufficiently different so that the effect of these two properties on

the di-electric strength would be evident.

Series F was constructed as follows:

No.	No.1 Tenn. Ball.Clay.	N.Carolina Kaolin.	Flint.	Calcined N.Carolina Kaolin.	$CaCO_3$
F	10	45	22	23	0
F1	"	"	"	22	1
F2	"	"	"	21	2
F3	"	"	"	20	3
F4	"	"	"	19	4
F5	"	"	"	18	5
F6	"	"	"	17	6
F7	"	"	"	16	7
F8	"	"	"	15	8

Series G(1 to 8) has $MgCO_3$ substituted for the $CaCO_3$ in series F.

Series H(1to8) has $BaCO_3$ substituted for the $CaCO_3$ in series F.

Series I has ZnO substituted for the $CaCO_3$ in series F.

The four series were burned to cone 13 and as only part of those containing $CaCO_3$ were vitrified it was thought useless to calculate more than the porosity and di-electric strength which was done with the following results:

No.	Por. in Percent.	Voltage per mm. #	No.	Por. in Percent.	Voltage per mm.
F	28.02	---	H1	24.91	---
F1	27.60	---	H2	24.62	---
F2	20.52	---	H3	17.68	---
F3	17.81	---	H4	14.80	---
F4	12.65	---	H5	12.43	---
F5	12.84	5,000	H6	13.44	---
F6	.05	6,000	H7	13.10	5,450
F7	.03	6,700	H8	11.65	5,400
F8	.06	8,000			
			I1	24.61	---
G1	26.12	---	I2	22.64	---
G2	25.80	---	I3	23.04	---
G3	25.04	---	I4	22.32	---
G4	24.32	---	I5	22.80	---
G5	23.90	---	I6	18.50	---
G6	23.30	---	I7	20.82	---
G7	25.04	---	I8	17.03	5,200
G8	26.92	5,020			

#Note-(Body tooweak to stand puncture test.)

The results show that six percent of $CaCO_3$ produces a non-porous body at this temperature which does not have a high di-electric strength and that each increase of $CaCO_3$ increases the strength.

$MgCO_3$ has failed to produce a perceptible effect upon the porosity. $BaCO_3$ decreases the porosity about one-half and eight percent has about the same effect as five percent of $CaCO_3$. ZnO has s small fluxing effect coming after $CaCO_3$ and $BaCO_3$.

The F series shows the remarkably sudden fluxing action of $CaCO_3$. F5 which contains 5% $CaCO_3$ has a porosity of 12.84% while F6, with 6% $CaCO_3$, is practically non-porous.

When the puncture tests of F6, F7,& F8 are compared with Spar porcelains having practically the same porosity it is readily seen that the feldspar bodies have a much higher di-electric strength.

General conclusions.

(1). For all practical purposes the Di-electric Strength may be considered as directly proportional to the Thickness.

(2). Insulators possess their maximum Di-electric Strength after becoming well vitrified which confirms the statement made by Bleininger and Stull (3) and burning to a higher temperature does not produce a perceptible change in their resistance to puncture until a vesicular structure begins to form.

(3). The method of firing Porcelain Insulators (rapid firing and quick cooling or slow burning and cooling) does not affect the di-electric strength.

(4). Insulators can be made from No.1 plastic and flint fire-clays which possess as high di-electric strength as white porcelains.

(5). The writer is of the opinion that Composition affects the di-electric strength of Insulators (all other things being equal) and expects some investigations, now in progress, will verify this opinion.

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